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**A NMR STUDY OF PENETRANT DIFFUSION IN NAFION AND THE
ASSOCIATED MORPHOLOGICAL STRUCTURE**

FINAL PROGRESS REPORT

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TABLE OF CONTENTS

Table of Contents	1
Project Abstract	2
Introduction	3 - 5
Experimental	5
Results and Interpretation	6 - 16
Discussion	17 - 21
References	22
Appendixes	23 - 24

- 1) Lists of manuscripts**
- 2) Scientific Personnel Supported**
- 3) Inventions**
- 4) Technology Transfer**

A NMR STUDY OF PENETRANT DIFFUSION IN NAFION AND THE ASSOCIATED MORPHOLOGICAL STRUCTURE.

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Abstract:

Pulsed field gradient NMR was used to determine the self diffusion constants for water and ethanol in Nafion (Dupont trademark) as a function of temperature and concentration. Typical values for water range from $3 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at a temperature of 300K and a concentration of 2.5 wt% water to $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at a temperature of 360K and a concentration of 24 wt%. The form of the concentration and temperature dependence of the self diffusion constants is typical of that expected from free volume theory but only some of the regions of the ionomer are expected to be involved in solvent transport. Fluorine -19 magic angle spinning spectra with side band suppression yielded high resolution Fluorine spectra at spinning speeds of 6KHz. Fluorine spin diffusion between resolved resonances was measured to obtain morphological information. Xenon-129 NMR was also used to probe the morphology. The apparent domain size associated with the resonance from the pendant ionomer side chain increases with solvent content and is greater in size in the case of ethanol compared to water. A picture of Nafion morphology as a bicontinuous phase structure is suggested.

Introduction.

The transport of ions through the perfluorosulfonate ionomer: Nafion (DuPont trademark) has been widely studied because of the electrochemical applications of this material in such areas as ion selective electrodes and fuel cells.^{1,2,3} The permeability of Nafion to low molecular weight gases has also been measured since membranes of this material also show selectivity again with possible applications. The transport of water, and low molecular weight alcohols across Nafion membranes has been observed to be very rapid which allows for the prospect of the separation of water from organic molecules which do not contain ionizable protons. However it is difficult to extract a diffusion constant from permeability measurements in a complex material like Nafion since a number of corrections are required. The permselectivity of Nafion with respect to hydrophilic versus hydrophobic penetrants suggests the potential application as a flexible barrier material for the soldier. Also Nafion represents a good model for the study of permselective behavior in general in a material of complex morphology.

Self-diffusion constants can be directly determined by pulse field gradient NMR measurements. Careful measurements of this type have been made for water in Nafion as a function of chemical activity. However a larger range of measurements as a function of temperature and concentration would be useful in order to consider the diffusion of water in terms of typical polymeric interpretational approaches involving free volume theory for concentration dependence and WLF for temperature dependence^{4,5} This approach is applicable for diffusion of a penetrant in a matrix undergoing segmental motion⁶. Free volume concepts would not be expected to apply to the viscoelastic response of bulk Nafion but they may allow for a reasonable interpretation of the environment experienced by a small solvent molecule diffusing through Nafion. The application of these interpretational approaches is complicated by the complex morphology of Nafion and by morphological changes induced by the addition of a strongly interacting solvent. To clarify this aspect, a morphological study based on fluorine-19 spin diffusion and Xenon-129 NMR was undertaken.

The self diffusion constant of ethanol is also considered here since it is comparable to that of water and the morphology of Nafion in the presence of ethanol is determined in the morphological study as well. Solvents are expected to produce morphological changes in the ionomer and each solvent can be expected to induce different changes. Thus it will be helpful to compare self-diffusion, morphology and then permeability. To achieve the latter comparison, permeability measurements were performed on the same commercial samples of Nafion and are reported elsewhere⁷. In the interpretation of permeability, it is helpful to have an independent measurement of the self-diffusion constant as well as morphological information.

The morphology of ionomers and Nafion is an area of considerable activity over the years and there has been an ongoing interplay of diffusion measurements and morphological measurements. The experimental approach that has had the most impact on the morphological models of Nafion and other ionomers is small angle X-ray scattering, SAXS. The salt forms of Nafion display an "ionic peak" which has been widely considered as a spherical cluster of cations and the associated anion from the pendant group of Nafion. Water and other hydrogen bonding solvents are sorbed into these clusters. However to account for rapid diffusion of water, the existence of channels between the clusters has been proposed. The channels have also been considered as the

source of selectivity in the transport of ions through Nafion. The material outside the clusters is considered to be largely composed of perfluorethylene groups which are present in both crystalline and amorphous forms. The cluster concept has been embellished over the years and various forms of this model could be used to interpret the volume fraction of clusters which support transport. Some local arrangement of the clusters relative to each other is required for this and one model uses spheres on a diamond lattice and allows for long range disorder.

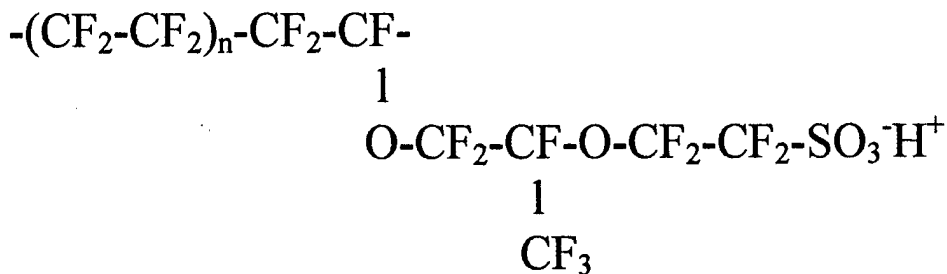
From the point of view of fluorine-19 spin diffusion measurements and xenon-129 chemical shifts there are two sorption environments in Nafion as in the cluster model. However, the NMR data does not require the existence of spherical clusters to be interpreted and indeed Eisenberg⁸ in reviewing the morphological studies concludes that the clusters could be a continuous phase and there is no evidence for the existence of channels. Thus for the purposes of interpreting the self-diffusion data of water and ethanol, a continuous phase consisting of pendant groups will be considered as the environment primarily supporting transport of water and ethanol. This environment will be considered as having a random spatial character. There is the possibility that the pathway for diffusion in such a system will be tortuous. Pulse gradient diffusion measurements can detect tortuosity⁹ since the apparent diffusion constant could depend on the overall time scale of the experiment. This is especially likely if the phase supporting transport is a minor component of the system. This experimental signature will be checked as measurements are made.

Why might free volume and WLF type behavior be encountered? In the pendant group phase in the presence of solvents, some part of the polymeric system could undergo local segmental motion. On the length scale of the penetrant, the friction experienced might then be similar to that of a swollen polymeric rubber undergoing segmental motion. Since the system as a whole does not consist of a single phase, the bulk response will not be that of a polymeric rubber but at the local level it may be a satisfactory approach. Tortuosity may enter the problem since the path length could be quite long in order for the solvent to diffuse over length scales greater than the morphological structure. Again the presence of tortuosity leads to an experimental signature in the PFG data and in relating self-diffusion to a property such as permeability this factor must be included.

For the determination of morphology fluorine-19 NMR presents an interesting opportunity because the large chemical shifts associated with this nucleus allow for the study of morphology based on the chemical structure of the ionomer. The disadvantage of fluorine-19 NMR is the broad line widths observed in the solid state which arise from the dipole-dipole interaction between fluorine-19 nuclei and from the large chemical shift anisotropy of this nucleus. Recently the technology associated with magic angle spinning has allowed for such rapid spinning that the dipole-dipole interaction and chemical shift anisotropy interaction can be averaged to their isotropic values producing essentially high resolution solid state NMR spectra¹⁰.

Under these conditions, chemical shift selection can be used to create magnetization gradients suitable for spin diffusion studies¹¹. This technique has been applied to a number of morphological problems in polymer science including ionomer blends.

The perfluorosulfonate ionomer, Nafion has the chemical structure:



The morphology can be studied by fluorine-19 NMR since the shift of the fluorines on the side chain with the sulfonate group leads to resonances which are well separated from the resonances of the perfluoroethylene groups in the backbone. Thus the proposed morphological features coincide nicely with the differences arising from fluorine-19 chemical shifts. Also solvents like water are only expected to enter the clusters and channels so these regions should selectively swell which can again be monitored by fluorine-19 NMR. Some reorganization of the morphology has been proposed in Nafion upon swelling¹² and the study of the morphology in the presence of two solvents, water and ethanol, may indicate the changes in morphology associated with different solvents.

The rotational mobility of the pendant groups and the backbone of the perfluorosulfonate ionomer is reflected in the static fluorine-19 line widths. Mobility of the polymer in the presence and absence of penetrants can affect spin diffusion. It is also a factor since it can influence the translational mobility of penetrants and it can be related to the extent of morphological rearrangement upon addition of penetrants.

The last morphological experiment included in this investigation will be xenon-129 NMR. Xenon-129 shielding is sensitive to the sorption environment in a variety of systems including polymers¹³. Xenon-129 NMR can help identify the number of domains that participate in the uptake and transport of a penetrant. Xenon gas is not likely to favor domains associated with ions and pendant groups over amorphous fluorocarbon regions so that both these types of domains may be detected. However, xenon is likely to be excluded from crystalline domains associated with the fluorocarbon backbone units of Nafion. If xenon-129 signals from different sorption environments are observed, two-dimensional exchange experiments can be used to detect transport of xenon from one domain to the other.

Experimental.

Nafion in the hydrogen form was purchased from Aldrich and has an equivalent weight of 1250 g per ionic unit. The Nafion was dried in a vacuum oven for several days

at a temperature of 80°C to remove most of the residual water. Known weights of either water or ethanol were then added to a sample of Nafion in an NMR tube which is then sealed. The sample was allowed to equilibrate at a temperature of 50°C for several days. After equilibration the diffusion constant measured did not change over a period of months. The Nafion was cryo-milled to produce a powder suitable for magic angle spinning experiments. The Nafion powder was swollen to different levels with deionized water or absolute ethanol. For the xenon-129 spectra, Nafion was placed in a sealed 10mm glass tube under a pressure of 12 atm of xenon gas.

All diffusion experiments were performed on a Bruker MSL 300 spectrometer with a high resolution gradient accessory and a gradient probe. The well known Stejskal-Tanner pulse sequence $\pi/2 - G(\delta) - \pi - G(\delta) - (\text{echo})$ was used to measure the diffusion constant of both water and ethanol. The stimulated echo sequence $\pi/2 - G(\delta) - \pi/2 - \tau - \pi/2 - G(\delta) - (\text{echo})$ was used when diffusion was slow and long times between gradient pulses were required. The strength of the magnetic field gradients was varied from 14 Gauss/cm to 140 Gauss/cm. The length of δ was in the range 1ms to 5ms and the time between gradient pulses, Δ , was in the range 3 to 600ms. The length scale of diffusion is microns given this time scale and diffusion constants in the range of 10^{-5} to 10^{-7} cm²/s.

All fluorine-19 NMR experiments were performed on a Bruker MSL 300 at a frequency of 288.4 MHz in a 4 mm MAS probe except for the magic angle spinning spectra taken at 35kHz which were acquired on a Bruker Avance 400 in a 2.5mm probe. The fluorine-19 spin diffusion measurement were made at a spinning speed of 5 kHz with care taken so that spinning side bands did not overlap the center band resonances involved in the magnetization exchange. The fluorine-19 $\pi/2$ pulse width was typically 3.2 μ s and a DANTE sequence was used to selectively invert one of the resonances in order to create a magnetization gradient. In the experiments reported here the OCF₂ and CF₃ resonances of the pendant group at -80 ppm relative to CFCI₃ were inverted and spin exchange to the CF₂ of the backbone at -120 ppm then occurred. A series of spectra were acquired as a function of time after the inversion to monitor the return to spin-spin equilibrium. Typically spin-spin equilibrium was reached in 50ms which was considerably shorter than the spin-lattice relaxation times which are the order of a second or longer. Static fluorine-19 spectra were taken in the magic MAS probe with the bearing pressure turned off to prevent spinning.

Xenon-129 experiments were performed on a Varian Unity 500 at 138.3 MHz. The typical $\pi/2$ pulse width is 21 μ s and recycle times of 60s were employed which are approximately three times the spin-lattice relaxation time. Two-dimensional exchange spectra were acquired to monitor exchange of sorbed xenon gas between sorption environments¹⁴. The total spectral width was set at 25 kHz with 64 data points in t_2 and in t_1 . Spectra were referenced by setting the free gas signal to 0 ppm.

Morphology: Results and Interpretation

In Figure 1, a static fluorine-19 spectrum of dry Nafion is compared with a MAS spectra taken with a 5kHz spinning rate with side band suppression using the TOSS

sequence and an 8 kHz spinning rate spectrum with side bands present. In Figure 2, a 35kHz spinning rate spectrum is presented.

In Figure 3, a static fluorine-19 spectrum is compared with water and ethanol swollen Nafion at several concentrations.

Figure 4 is standardized spin diffusion plot following the form suggested by VanderHart and McFadden¹¹. In this example the change of the normalized pendant group magnetization is plotted against the square root of time after the DANTE inversion. The initial linear region is fit to a straight line which is extrapolated to zero intensity to determine the intercept on the square root of time axis which is the parameter $t_{sd}^{1/2}$. Tables I and II reports values of $t_{sd}^{1/2}$ as a function of water and ethanol concentration.

Figure 5 is a two-dimensional xenon-129 spectrum for a sample of Nafion under 12 atm of xenon gas.

Fig.1

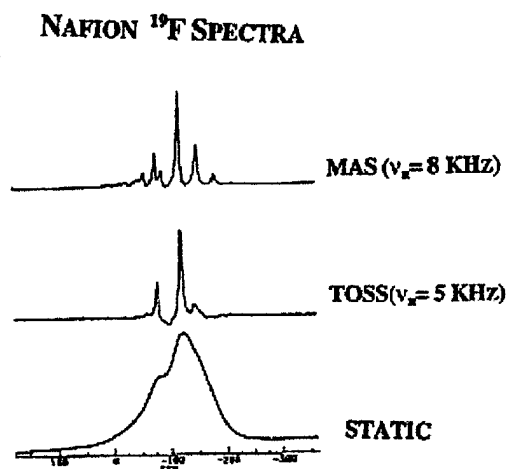


Fig.2

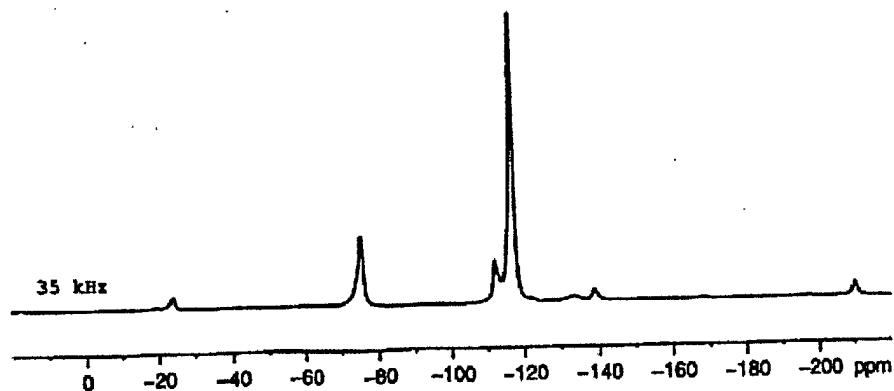
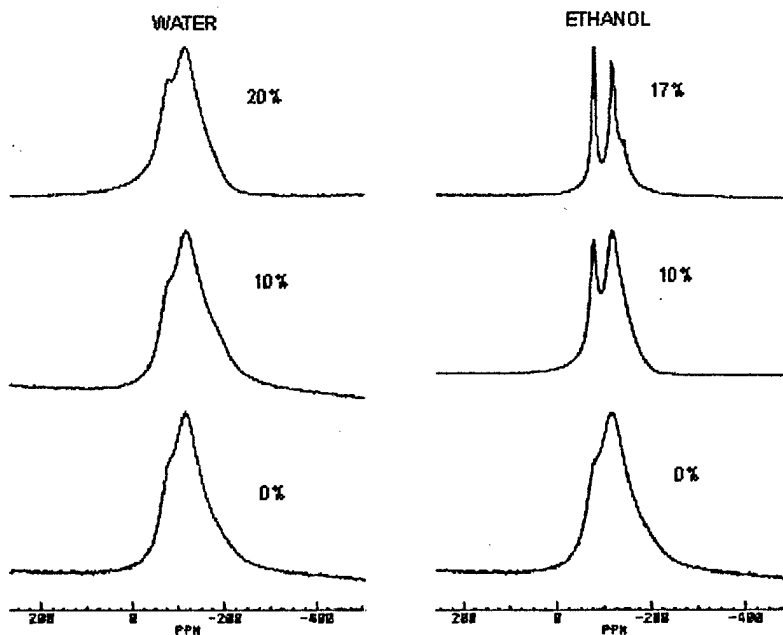


Fig.3



The fluorine-19 spectrum taken at 35kHz shown in Figure 2 has 5 resolved resonances that can be largely assigned following the earlier structural study of Schick, Gebel, Pineri and Volino¹⁵. The small signal at -146 ppm relative to CCl_3F corresponds to the CF groups in the back bone and in the pendant group. The second small resonance at -139 ppm corresponds to the CF_2 adjacent to the sulfonate group. The large resonance at -120 ppm arises from the CF_2 groups in the backbone. The smaller signal at -115 ppm which overlaps the backbone CF_2 resonance corresponds to backbone CF_2 groups which are adjacent to the backbone CF group to which the pendant group is attached. This last assignment is slightly different from that given earlier and is based on the relative intensity of the signals at -115 and -120 ppm. The last resonance at -75 ppm arises from the CF_2 and CF_3 groups on the side chain.

Following VanderHart and McFadden¹¹, the repeat length, L , of the morphological structure can be calculated from the parameter $t_{sd}^{1/2}$ derived from plots such as that shown in Figure 4. In this interpretation, two types of domains are assumed: one of which is made up of the pendant groups and one of which is made up of the backbone CF_2 groups. A one dimensional interpretation is chosen, though the structure is certainly not simple lamellar, since spin diffusion data provides little information on the dimensionality of the morphology. The equation relating L to $t_{sd}^{1/2}$ is

$$L = [4(t_{sd}^{1/2})(D_A D_B)^{1/2}(\rho^{F_A} f_a + \rho^{F_B} f_b)] / [f_A f_B \pi^{1/2}(\rho^{F_A} D_A^{1/2} + \rho^{F_B} D_B^{1/2})] \quad (1)$$

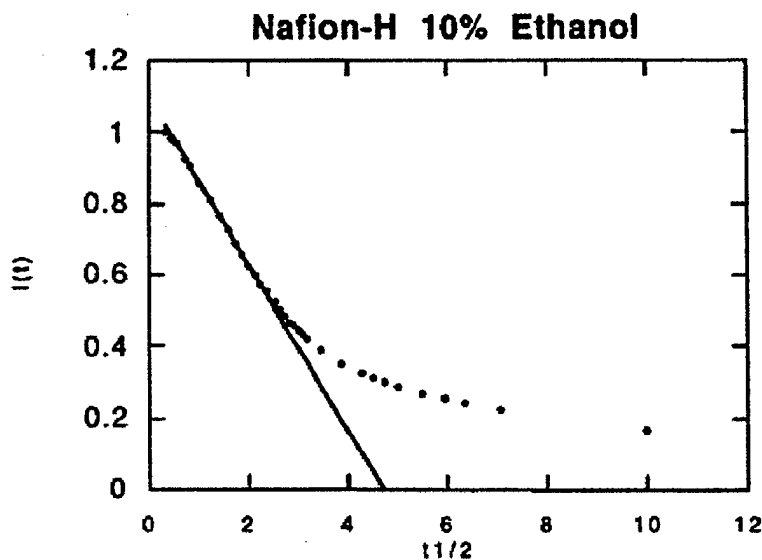
where ρ^{F_A} is the fluorine-19 spin density in domain A, ρ^{F_B} is the fluorine-19 spin density in domain B, D_A is the spin diffusion constant in domain A, D_B is the spin diffusion constant in domain B, f_A is the volume fraction of domain A and f_B is the volume fraction of domain B. Note that the symbol F refers to fluorine in this equation.

The pendant group domain will be considered as the A domain and the backbone group domain will be considered as the B domain. The domain size is given by the product of f and L . For dry Nafion, the volume fraction corresponds to the weight of the pendant group, 363, divided by the equivalent weight of 1250. For the swollen Nafion, the volume associated with a weight of pendant chain is calculated assuming a density of 2.0g/cm^3 . The same density is used for the backbone domains. Simple additivity of volumes is assumed so that

$$f_a = (V_{\text{solvent}} + V_{\text{pendant}}) / (V_{\text{solvent}} + V_{\text{pendant}} + V_{\text{backbone}}) \quad (2)$$

This equation also assumes that all of the water or ethanol is in the pendant group domain. The spin diffusion constant will be assumed as $0.62\text{nm}^2/\text{s}$ which is the value for a rigid organic hydrocarbon¹¹ given that fluorine interatomic distances are similar in fluorocarbons and hydrocarbons as are the gyromagnetic ratios. Table I lists the parameters used to calculate domain sizes as well as the sizes obtained by substituting these values in equation 1.

Fig.4



Some investigators¹⁶ reduce the spin diffusion constant in semi-solid systems where there is limited molecular motion. The effect of this possibility can be considered since the usual form of the relationship is

$$D_i = K / T_{2i} \quad (3a)$$

where K is a constant and T_{2i} is the spin-spin relaxation time of one of the domains. Recently Mellinger, Wilhelm and Spiess suggested a linear form of this equation

$$D_i = (K / T_{2i}) + b \quad (3b)$$

where b is a positive intercept. There is little molecular motion in dry Nafion so this system will be used to set the constant K . The systems swollen with water narrow rather little as can be seen in Figure 3 so lower values of the spin diffusion constant need not be considered but the ethanol swollen systems show much narrowing as can also be seen in Figure 3. Values of T_{2i} can be estimated by fitting the ethanol swollen spectra in Figure 3 to a combination of Lorentzian and Gaussian line shapes. For the ethanol swollen spectra, each resonance is centered at the isotropic shift value determined from high speed magic angle spinning spectra. The relative fluorine populations of the each resonance are known from the structure and are therefore also fixed. The swollen spectra are fit and the relevant line width parameters are given in Table II. The dry spectrum is fit with a series of Gaussians centered at each of the resolved resonance positions obtained from the high speed MAS spectrum except for one Lorentzian positioned at -120 ppm which corresponds to the amorphous backbone units which are somewhat mobile. All the Gaussians for the dry sample were given the same width though the populations of the the resonances at -80 , -115 and -120 ppm are weighted as a group by the repeat unit structure relative to the resonances at -139 and -146 ppm. The latter two resonances are small and are not resolved at all in the dry spectrum so they are inserted at the known position with the known relative weighting. The Gaussians are only an approximation of the true line shape since the more rigid lines result from both the dipole-dipole interactions and chemical shift anisotropy interactions. Using this line width fitting approach, estimates of T_{2i} are obtained which can be used to determine a level of line narrowing relative to the dry state. Assuming that the dipole-dipole contributions to the line width narrow to about the same extent as the chemical shift anisotropy contributions, the relative level of dipole-dipole reduction pertinent to the spin diffusion problem can be considered.

An examination of the relative T_{2i} estimates in Table II show that the resonances associated with the pendant group at -80 ppm narrow by about an order of magnitude. The backbone CF_2 resonances at -115 and -120 ppm are not resolved in either the dry or swollen static spectra. They should be fit by a single line width parameter based on the repeat unit structure but actually two different line components are required. The origin of the two are associated with the morphological characteristics of the backbone domains which are partially crystalline. Arbitrarily the resonance at -115 ppm is fit as a broad Gaussian which does not narrow with the addition of ethanol in the simulations of the two swollen spectra. This line shape component is identified with the crystalline regions of the backbone domain. The other component is a narrower Lorentzian positioned at -120 ppm which is identified with the amorphous component of the backbone domains. In the swollen spectra, the intensities of these two backbone components are equal indicating crystallinity of about 50% of the backbone domain. The amorphous component of the backbone resonance narrows by less than a factor of two in going from dry Nafion to 17% ethanol. These simulations are consistent with the interpretational approach used here which assumes that the ethanol is primarily located in the pendant group domain.

The question remains whether it is helpful to scale the spin diffusion constants according to eqs. 3a or 3b. First there is rather little narrowing associated with the backbone domain so scaling seems unnecessary for this component. The pendant group resonance at -80 ppm does narrow by a factor of almost 10 but the apparent $1/T_2$ for this

resonance is still 6 kHz. According to Mellinger, Wilhelm and Spiess for protons if $1/T_2$ is 1 kHz or larger the spin diffusion constant is reduced by less than a factor of 3. In our case the true fluorine dipolar $1/T_2$ value is going to be appreciably less than the apparent value of 6 kHz but probably no smaller than 1 kHz. Given all the complexities of Nafion, the best course of action would seem to be to use a single value of D associated with a rigid system which leads to the values for domains given in Table I.

Table I: Domain Size Determinations from ^{19}F Spin Diffusion Measurements

% Penetrant	$t_{sd}^{1/2} \text{ (ms)}^{1/2}$	f_a	L (nm)	Pendant Domain Size (nm)
0	2.569	0.332	11.44	3.80
10 (H ₂ O)	2.730	0.453	10.13	4.59
20 (H ₂ O)	3.443	0.555	11.83	6.56
10 (EtOH)	4.682	0.479	16.93	8.12
17 (EtOH)	5.604	0.561	19.14	10.74
40 (EtOH)	10.773	0.752	37.74	28.39

Table II Line Shapes and Apparent Values of $1/T_2$ from Line Shape Simulations

Ethanol Conc.	$1/T_2$ (kHz)				
(wt%)	-80 ppm	-115ppm (amorphous)	Resonances -120ppm (crystalline)	-139ppm	-146ppm
0	Gaussian 57	Lorentzian 22	Gaussian 57	Gaussian 57	Gaussian 57
10	Lorentzian 12	Lorentzian 22	Gaussian 57	Lorentzian 22	Lorentzian 22
17	Lorentzian 6.2	Lorentzian 14	Gaussian 57	Lorentzian 14	Lorentzian 14

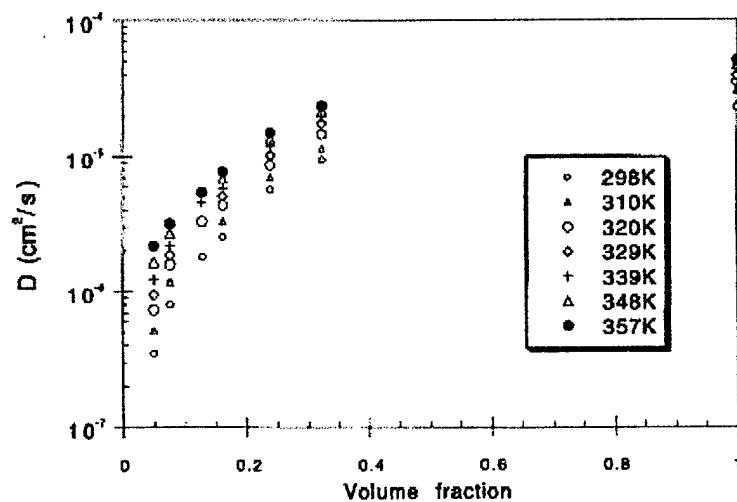
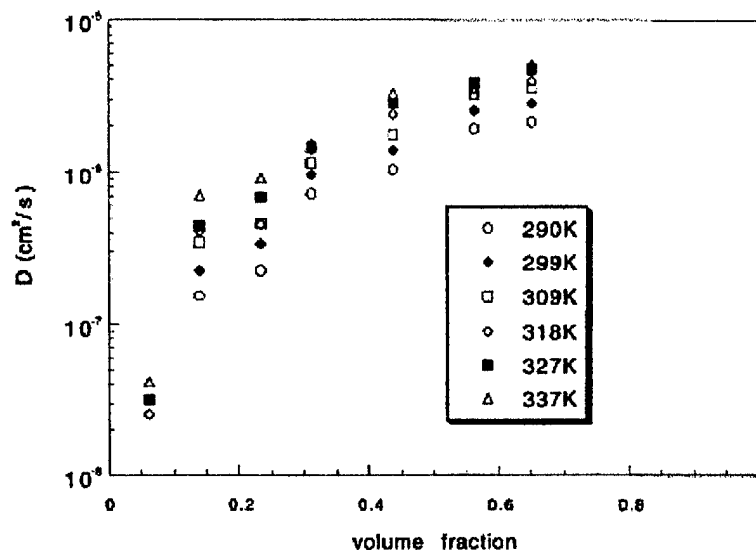


Fig.7



The concentration dependence of the diffusion coefficients at a given temperature can be expressed using Fujita free volume theory⁴ as

$$\ln \frac{D}{D_0} = \frac{\left(\frac{f_s}{B_d} - \frac{f_p}{B_d}\right)\phi_s}{\left(\frac{f_p}{B_d}\right)^2 + \left(\frac{f_p}{B_d}\right)\left(\frac{f_s}{B_d} - \frac{f_p}{B_d}\right)\phi_s} \quad (4)$$

where f_p is the fractional free volume of the polymer, f_s is the fractional free volume of the solvent, B_d is the minimum hole size needed to allow for the molecule in question to undergo displacement, and ϕ_s is the volume fraction of the penetrant.

In the case of a two phase system such as Nafion where the penetrant is present mainly in only one phase, the volume fraction of the penetrant will be calculated based on only that fraction of the Nafion volume which is accessible to the penetrant. To a first approximation the accessible volume for either water or ethanol would be the volume of the pendant group phase. This view of the swelling process in Nafion was used in the interpretation of the fluorine-19 spin diffusion study of morphology and it led to a consistent view of the changes upon the addition of a penetrant and also indicated important differences between water and ethanol.

For dry Nafion the pendant group domain will be considered to have a volume fraction corresponding to the weight of the pendant group, 363, divided by the equivalent weight of 1250. For the swollen Nafion, the volume associated with a weight of pendant chain is calculated assuming a density of 2.0g/cm³.

$$\phi_s = (V_{\text{solvent}}) / (V_{\text{solvent}} + V_{\text{pendant}}) \quad (5)$$

Table III lists the weight fraction water, volume fraction water considering the total weight of Nafion and the parameter ϕ_s as defined above.

Table III: Concentration of Water in Nafion for Diffusion Measurements

Weight Fraction	Volume Fraction	ϕ_s
0.0253	0.0494	0.148
0.0394	0.0758	0.215
0.0685	0.1282	0.329
0.0876	0.1611	0.390
0.1312	0.2320	0.502
0.1570	0.2390	0.511
0.1929	0.3234	0.614

Figure 8 displays sample fits of the diffusion data as a function of the concentration variable ϕ_s using equations 4 and 5 at a series of temperatures. The parameters of the fit are D_o , f_p/B_d and f_s/B_d and the resulting values of these parameters are shown in Table IV.

Fig.8

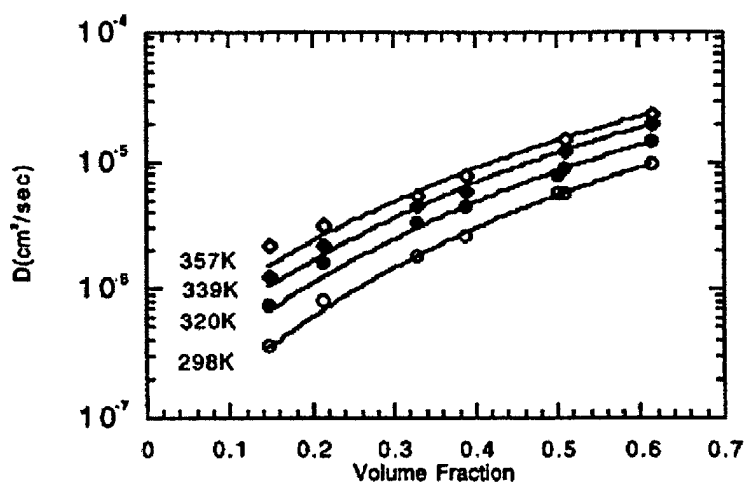


Table IV Free Volume Parameters for Water in Nafion

T(K)	$D_o(\text{cm}^2/\text{s})$	f_p/B_d	f_s/B_d
298	4.46×10^{-8}	0.089	0.222
310	6.26×10^{-8}	0.091	0.225

320	1.14×10^{-7}	0.093	0.220
329	1.25×10^{-7}	0.091	0.211
339	1.92×10^{-7}	0.096	0.222
348	2.50×10^{-7}	0.098	0.225
357	3.27×10^{-7}	0.101	0.230

The same procedure can be applied to the concentration dependence of the self diffusion constants for ethanol in Nafion. First the concentration parameters for the ethanol measurements are listed in Table V.

Table V Concentration of Ethanol in Nafion for Diffusion Measurements

Weight Fraction	Volume Fraction	ϕ_s
0.0252	0.062	0.1810
0.0590	0.1385	0.3489
0.1476	0.3093	0.5989
0.2314	0.4359	0.7203
0.3333	0.5619	0.8105
0.4198	0.6499	0.8609

A free volume fit of the concentration dependence is then performed using ϕ_s as the relevant variable. The parameters of the fit are listed in Table VI.

Table VI Free Volume Parameters for Ethanol in Nafion

T(K)	D_0 (cm ² /s)	f_p/B_d	f_s/B_d
290	1.0×10^{-9}	0.070	0.166
299	2.0×10^{-9}	0.072	0.163
309	3.0×10^{-9}	0.072	0.158
318	4.0×10^{-9}	0.080	0.198
327	5.0×10^{-9}	0.078	0.182
337	6.0×10^{-9}	0.087	0.227

The temperature dependence of the self diffusion constants at a given concentration can be analyzed using the following form of the WLF equation ^{5,17}.

$$\ln\left(\frac{DT_0}{D_0T}\right) = \frac{\frac{\alpha(\phi_s)}{B_d}(T - T_0)}{\frac{f(\phi_s)}{B_d} + \left(\frac{f(\phi_s)}{B_d} + \frac{\alpha(\phi_s)}{B_d}(T - T_0)\right)} \quad (6)$$

where $f(\phi_s)$ is the fractional free volume of the solution, $\alpha(\phi_s)$ is the fractional free volume expansion factor and T_0 is the reference temperature. The diffusion constants plotted as a function of temperature and the corresponding fits according to eq 6 are shown in Figure 9 for water. The parameters of the fits are given in Table VII for water and Table VIII for ethanol.

Fig.9

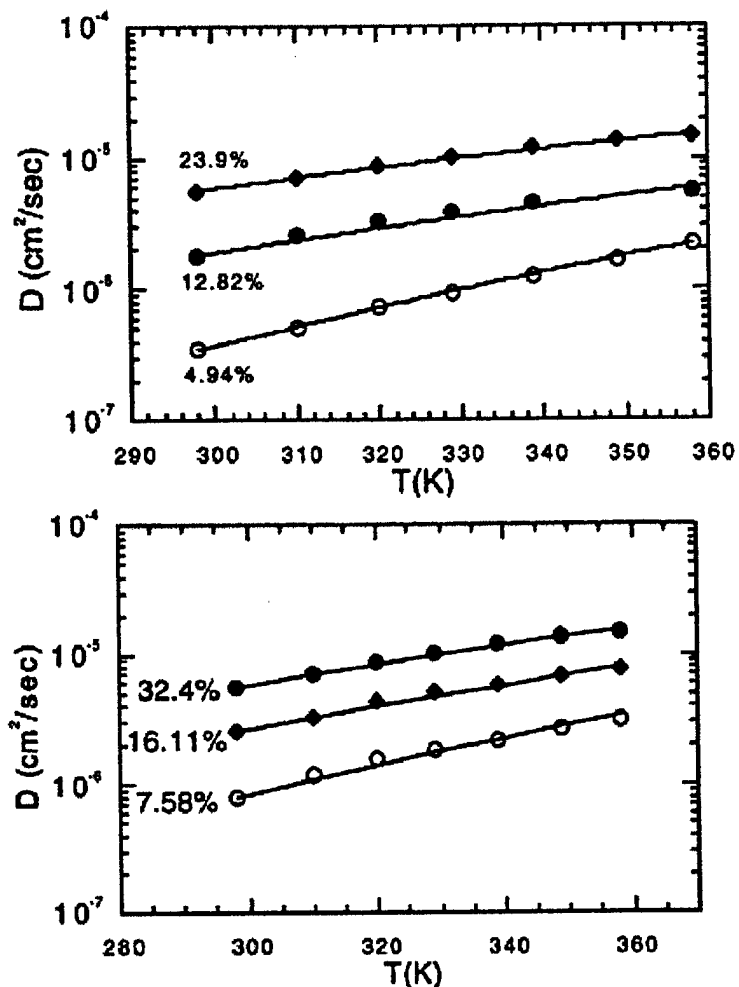


Table VII WLF Parameters for water in Nafion

ϕ_s	$f(\phi_s)/B_d$	$\alpha(\phi_s)/B_d$
0.148	0.075	1.78×10^{-4}
0.215	0.122	3.52×10^{-4}
0.329	0.137	3.60×10^{-4}
0.390	0.171	5.55×10^{-4}
0.511	0.218	7.70×10^{-4}
0.614	0.279	1.27×10^{-3}

Table VIII WLF Parameters for Ethanol in Nafion

ϕ_s	$f(\phi_s)/B_d$	$\alpha(\phi_s)/B_d$
0.181	0.049	5.48×10^{-5}
0.349	0.079	2.02×10^{-4}
0.599	1.140	0.059
0.720	0.358	0.004
0.811	1.650	0.203
0.861	0.558	0.008

Discussion

To interpret the spin diffusion observed when the fluorine-19 resonance is inverted, the assumption is made that the pendant group constitutes a distinct domain separate from a domain consisting of perfluoroalkane groups associated with the polymer backbone. This assumption is consistent with the general picture of ionomers^{1,2} and appears to lead to meaningful results in the case of spin diffusion data on Nafion. Spin diffusion indicates domains in the dry and swollen systems are in the nanometer range. This is a larger dimension than that associated with chemical structure indicating that there is an aggregation of pendant groups. The actual size of several nanometers is comparable to the size of clusters seen by SAXS in salt forms of ionomers^{1,2}. The spin diffusion results tell little of the shape or dimensionality of the aggregates. Thus the presence or absence of spherical clusters connected by channels is not demonstrated. However, the NMR results presented here require only two phases to be interpreted. The spin diffusion data do indicate the presence of some interface since the spin diffusion plots as shown in Figure 4 usually have a curvature at short times before the linear portion of the magnetization equilibration is reached in the plots of magnetization change versus the square root of time.

The xenon-129 two dimensional spectra also indicate only two overlapping environments. The sharper peak at 96 ppm coincides with that seen in poly(perfluoroethylene) and is assigned to an amorphous poly(perfluoroethylene) environment¹⁸. The second resonance at 103 ppm is assigned to domains containing the pendant group including the sulfonate functionality and hydrogen ion. This domain is more heterogeneous as indicated by the breadth of the line which is consistent with a domain containing the pendant group since this group is comprised of several different chemical groups. While two domains are described as containing either pendant groups or backbone groups, there is undoubtedly some mixing. The level of mixing is not known but the xenon-129 signals overlap indicating that the environmental influence on the xenon shielding has no sharp boundary. On the other hand there are definitely two distinguishable environments affecting the xenon-129 shielding.

In the 2D spectrum shown in Figure 5, off diagonal intensity represents exchange between different sorption environments by translational diffusion. Most of the diagonal intensity is centered around each of the two diagonal peaks. The peaks are heterogeneous in nature so this off diagonal intensity represents exchange within the heterogeneous environment of one or the other of the domains. For the mix time shown of 1 ms, there is a small amount of off diagonal intensity appearing associated with exchange between the two peaks. It manifests itself as a small change in the contour levels at a position corresponding to the intersection of lines drawn from the diagonal maxima of each of the two peaks associated with the two environments. This onset of exchange allows for an estimate of the average effect diffusion constant for xenon, D_{Xe} , in Nafion. Using the equation

$$D_{Xe} = b^2 / 6t_{mix} \quad (7)$$

where b is the domain size and t_{mix} is the mix time. If a value of $b = 5$ nm is chosen for dry Nafion, then D_{Xe} is $4 \times 10^{-11} \text{ cm}^2/\text{s}$ which is two orders of magnitude slower than the value determined for Xe in poly(styrene)¹⁹.

From the NMR data presented, one need only assert that there are two domains with no further structure than the presence of some interface between the domains. The rapid long range transport of water and low molecular weight alcohols argues that the domain which supports this transport must be continuous with rather little tortuosity. The diffusion results then adds one further point to the description of the morphology: the pendant group domain must be continuous. The simplest structure consistent with the NMR data and the presence of rapid long range diffusion of water and alcohols would be a random morphology with the pendant group domain being continuous.

This differs pictorially from the spherical clusters and channels. However Eisenberg²⁰ in a review concludes that there is no evidence for channels other than the need to explain the rapid transport of water. This author also states that the ionic clusters may actually be a continuous phase without a particular shape. From the point of view of the NMR data, a random continuous phase largely composed of ionomer side chains is all that is required. The second perfluoroalkane phase must be random if the other phase is random but the second phase may or may not be continuous. This could be established by studying the transport of species which are selectively sorbed into this phase.

As Nafion is swollen with either water or ethanol, the value of $t_{sd}^{1/2}$ increases indicating slower spin diffusion which is attributed to growth in the domain associated with the pendant group. The overall periodicity increases with addition of solvent and the size of the pendant group domain increases according to the assumptions and eq. 1. The size of the domain associated with backbone units increases more slowly. Even at an ethanol concentration of 40% where the pendant group domain is an order of magnitude larger, there is only a fractional increase in the backbone fluorocarbon domain. This is at least consistent with the assumption that these solvents are selectively sorbed into the pendant group domain.

Ethanol induces greater overall periodicity and correspondingly larger pendant group and backbone domains. There may be several inter-related reasons why ethanol has the ability to produce more reorganization of the morphology than water. One is the increase in T_2 which is significantly greater for ethanol relative to water as can be seen in

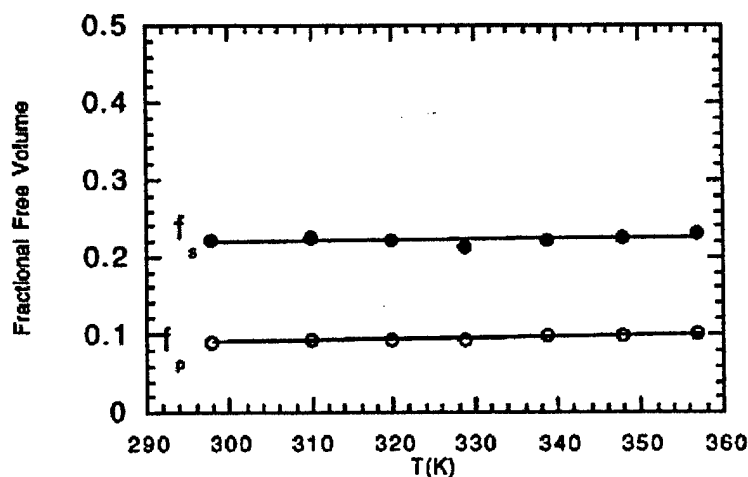
Figure 3. The increased rotational mobility of the backbone units and especially the pendant groups induced by ethanol is likely related to the increased morphological reorganization. Another aspect of the local mobility and morphological reorganization is the difference in the ability of ethanol to dissolve in the pendant group domain. The perfluoroether functionalities of the pendant group are more compatible with ethanol than water. This allows for the greater uptake of ethanol over water and the better plasticization of the pendant group. Water is a good solvent for the acidified sulfonate group but not the rest of this ionomer.

Once the reorganization is produced at the lowest concentration studied, then the backbone domain no longer grows rapidly and only the pendant group domain increases significantly in size as more solvent is added. Thus the initial introduction of ethanol or water produces most of the reorganization.

If the change in mobility as determined by the apparent T_2 is used to lower the spin diffusion constant D according to eq. 3, the periodicity and domain is somewhat reduced. However, the trends remain generally the same.

A Fujita type free volume analysis considering only the pendant group domain as accessible to the penetrant appears to yield a reasonable description of the experimental diffusion data and normal free volume parameters. The parameter for the polymer f_p/B_d is about 0.09 to 0.10 when water is the solvent and 0.07 to 0.09 when ethanol is the solvent. For comparison a study of the diffusion of toluene in poly(isobutylene) was made by pulse field gradient NMR and a similar analysis was performed as a function of concentration and temperature. Of course in that case all the polymer volume is considered as accessible and there are no strong interactions between solvent molecules or between solvent molecules and functional groups on the polymer. For poly(isobutylene), f_p/B_d varied from 0.09 to 0.14 over a temperature range comparable to this study of Nafion. Thus considering the diffusion of water and ethanol in Nafion to be controlled by polymer chain dynamics (free volume) leads to sensible parameters in spite of the potential for effects such as hydrogen bonding and ionization to complicate matters. Similarly, the free solvent volume parameter f_s has typical values as well; about 0.22 for water and 0.17 to 0.23 for ethanol. These are again much like the values determined for organic solvents in largely hydrocarbon based polymers.

Fig.10



If the polymer fractional free volume parameters determined from the concentration dependence of self diffusion are plotted as a function of temperature as shown in Figure 10, and then fitted to an equation of the form

$$f_p(T) = f_p(T_0) + \alpha_p(T - T_0) \quad (8)$$

where α_p is the thermal expansion coefficient for the polymer. A value of 9.1×10^{-5} is obtained when water is the solvent and this value is again of reasonable magnitude. Likewise, the value for the solvent thermal expansion coefficient can be determined and for water the value is 1.7×10^{-4} .

All of the free volume analysis performed and discussed here is based on water and ethanol only accessing the pendant group domain. The volume of the pendant group domain was determined by the weight fraction of the polymer that is pendant group. This approach was used because the morphological interpretation of swelling based on fluorine-19 spin diffusion led to reasonable results using this assumption and no assumption of geometrical shape was required. However one might use one of the typical cluster pictures. For instance, the original cluster model of Gierke and Hsu²¹ calculates the diameter of a cluster to be 3.88 nm with a Bragg spacing of 4.55 nm. For purposes of discussion, they employ a simple cubic lattice to array the clusters. One can calculate the volume fraction of the system that is clusters to be 0.32. This was for the same equivalent weight Nafion as studied here at a weight fraction water of 0.15. If the volume fraction is calculated following the approach employed to interpret the NMR data which assumes that the volume fraction is that of water plus the pendant group, then this becomes a volume fraction of 0.48. Essentially the difference leading to the two estimates of the accessible volume fraction is that the Gierke and Hsu model only includes the SO₃ group in the cluster while the whole pendant group is included in the accessible volume in the interpretation of the NMR data. Other interpretations²² consider the water itself to be the cluster in the interpretation of SAXS and SANS (small angle neutron scattering) and the accessible volume fraction is just the volume fraction of water. If none of the Nafion is assumed to be in the cluster or only a little of the Nafion is in the cluster (just the SO₃ groups), then a fit of the diffusion data as a function of concentration using Fujita free volume equations does not lead to reasonable free volume parameters. To get reasonable free volume parameters one must assume that 30 to 40% of the Nafion is in the cluster which is roughly the fraction of the system which is pendant group. Of course some of the polymer must be in the cluster to have a free volume type dependence since it assumes that segmental motion of a piece of the polymer controls the friction experienced by the penetrant. A large accessible volume fraction is also consistent with lack of any evidence of significant tortuosity in the pulse field gradient diffusion measurements. Of course the fractal character of the domain through which diffusion proceeds is also relevant. The method used here to estimate the accessible volume fraction is simplistic and should not be regarded as precise. It is arbitrary to include the pendant group but not the part of the backbone to which the pendant group is attached. There is likely to be disorder in the sense that in some cases some backbone units are in the accessible domain and in some cases perhaps only the ionizable group is in the accessible domain. Also ethanol appears to plasticize Nafion more readily producing larger domains. Perhaps a different choice of the fraction of the polymer to be considered

in the accessible domain should be made for ethanol. However such refinements cannot be made quantitatively without a better rationale for the definition of accessible volume.

The WLF parameters listed in Tables VII and VIII for water and ethanol respectively are again plausible values at least qualitatively consistent with the Fujita fitting based on concentration. An activation energy can be calculated from the WLF parameters using the relationship

$$E_D = \frac{R(298)^2 \frac{\alpha(\phi_s)}{B_D}}{\frac{f^2(\phi_s)}{B_D^2}} \quad (9)$$

The resulting values of E_D are given in Table VII. One could also assume an Arrhenius temperature dependence and analyze the self diffusion constants as a function of temperature using the equation

$$D = D_0 \exp\left(-\frac{\Delta H_D}{RT}\right) \quad (10)$$

Values of E_D are also included in Table IX.

Table IX Activation Energy Values

ϕ_s	$\Delta H_D(\text{kJ/mole})$	$E_D(\text{kJ/mole})$
0.148	26.9	23.2
0.215	19.8	17.5
0.329	19.1	14.1
0.390	16.4	14.0
0.511	14.6	11.9
0.614	13.9	12.0

Conclusions

The acidified form of the perfluorosulfonate ionomer Nafion displays a two phase morphology based on fluoroine-19 spin diffusion measurements. A two phase morphology is also consistent with the xenon-129 NMR spectrum. One of the domain consists primarily of pendant groups containing the ionomer functionality and the other domain is primarily composed of perfluoroethylene backbone groups. The size of both domains is in the nanometer range and a random shape is sufficient to explain the spin diffusion data. The addition of ethanol or water increases the periodicity mainly by increasing the size of the pendant group domain. Ethanol causes an increase of local mobility of the pendant groups and to a lesser extent the backbone groups. Water has less of an effect on local

mobility. Ethanol induces the creation of larger domains relative to both the dry form of Nafion and water swollen Nafion. The pendant group domain is continuous since there is rapid transport of either water or ethanol.

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(1) List of manuscripts:

1. "Xenon-129 NMR as a Probe of Solid Polymer Sorption Sites: A new View of Structure and Transport" J. M. Koons, W-Y. Wen, P.T. Inglefield, A. A. Jones. PMSE Proceedings, ACS 76, 433 (1997)
2. "Xenon-129 NMR as a Probe of Solid Polymer Sorption Sites: A new View of Structure and Transport" J. M. Koons, W-Y. Wen, P.T. Inglefield, A. A. Jones. ACS Symposium Series: Structure and Properties in Glassy Polymers. 710, 394, (1998)
3. "An NMR Study of the Diffusion of Water in Nafion and the Associated Morphological Structure" G. Meresi, A. Tao, X. Gong, W-Y Wen, P. T. Inglefield, A. A. Jones and N. S. Schneider. Polymer Preprints, 39, 886 (1998)
4. "Morphology of Dry and Swollen Perfluorosulfonate Ionomer by Fluorine-19 MAS NMR and Xenon-129 NMR", G. Meresi, Y. Wang, P. T. Inglefield and A. A. Jones (in preparation)
5. "Self-Diffusion of Water and Ethanol in Perfluorosulfonate Ionomer by Pulse Field Gradient NMR", X. Gong, A. Bandis, A. Tao, G. Meresi, P. T. Inglefield and A. A. Jones (in preparation)

(2) Scientific Personnel Supported:

Principal investigators:	Paul T. Inglefield, Alan A. Jones and Wen-Yang Wen
Post-Doctoral Fellows:	Ghirmai Meresi and Athinodoros Bandis
Research Assistants:	Yingzi Wang and Steve Gong
Consultant:	Nathan Schneider (Natick Army Lab.)

(3) Inventions: none

(4) Technology Transfer:

Our relation with the Army has been with the US ARMY NATICK R, D&E CENTER and with the personnel in the Survivability Directorate supervised by Don Rivin as well as other staff scientists at Natick. A list of the participants and there roles in relation to this work as well as some other areas of contact follow. Our contacts have been on essentially a weekly basis and a graduate student, Steve Gong, has been assigned to do some permeation measurements on apparatus available at Natick under the supervision of Nathan Schneider and Cy Kendrick. During the past year there have been meetings both at Natick and Clark which have involved presentations both reviewing the existing literature and discussing our own results. Attendance at these meetings consists of the Natick scientists as well as the Clark polymer research group including the PI's, post doctoral fellows and graduate students supported by the grant.

Don Rivin: Leader of the Survivability Directorate.

Since becoming involved in our discussions of Nafion there has been a considerable increase on Don Riven's part in interest in Nafion relative to other permselective membrane materials which were being studied previously. At this time Nafion is considered to be a good candidate for research as a model for the understanding of permselective membrane materials. A number of techniques are being applied by

different investigators at Natick and the results will be shared with the Clark group in a collaborative fashion.

Nathan Schneider: Associate of the Natick Lab., consultant on the ARO grant.

Nathan Schneider is the main liaison person between the Natick Lab. and the Clark research group. We have had an ongoing relationship with him back to his years as a scientist at the Army Materials Lab. at Watertown. This stems from his long term interest in penetrant diffusion in polymers. In conjunction with Cy Kendrick he has been involved in the obtaining and analyzing the permeation and sorption data of water in Nafion. He has been in charge of the grad. student, Steve Gong, who made these measurements including organics in Nafion to parallel his NMR PFG measurements of D at Clark. Our contacts with Nathan Schneider are on a weekly basis.

Cy Kendrick: Scientist at the Natick Lab.

He is responsible for the steady state permeation measurements on water in Nafion, which were used to compare with the NMR data (see above)

JoAnn Ratto: Polymer Research Engineer at the Natick Lab.

She is involved in the thermal and mechanical characterization work and has considerable experience and an ongoing interest in Nafion. Part of her PhD work was in the laboratory of Ferdinand Volino at Grenoble, France, who is responsible for some of the early NMR research on Nafion swollen with various solvents. JoAnn Ratto has collaborated with our group for a number of years providing thermal and mechanical expertise to supplement our NMR experiments.

Dianne Steeves: Scientist at the Natick Lab.

Dianne Steeves is, in addition to her status at the Natick Lab., is a part-time Graduate student in Chemistry at Clark in our NMR/Polymer research group. She also is the NMR spectroscopist at Natick and she is the point of contact for NMR service which we provide for Natick on an ongoing basis since they no longer have any NMR capabilities on site. She provides analytical and research level NMR using the instrumentation at Clark and is involved in research projects at Natick independent of the Nafion work, for example in an ongoing project on the structure of natural and synthetic silk materials and a project involving non linear optical materials. Some of this work is supported by a small service contract(#DAAN02-98-P-8132) between Natick and Clark University.